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Recent experiments show that the anisotropy of the optical second harmonic (SHG) response from noble metal surfaces persists at frequencies below those associated with interband transitions and plasma resonances. It is proposed that for noble metals this anisotropy is a consequence of the hybridization between s- and d-orbitals. By taking advantage of a moment expansion and related path counting methods, the relative importance of the different contributions to SHG can be identified. To illustrate this result, the nonlinear polarizations are calculated using the recursion method.

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**"S-d Hybridization and Anisotropy of the Optical Second Harmonic at Low
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S-d Hybridization and Anisotropy of the Optical Second Harmonic at Low Frequencies

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Abstract

Recent experiments show that the anisotropy of the optical second harmonic (SHG) response from noble metal surfaces persists at frequencies below those associated with interband transitions and plasma resonances. It is proposed that for noble metals this anisotropy is a consequence of the hybridization between s- and d-orbitals. By taking advantage of a moment expansion and related path counting methods, the relative importance of the different contributions to SHG can be identified. To illustrate this result, the nonlinear polarizations are calculated using the recursion method.

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Recent optical second harmonic generation (SHG) studies of single crystal metal surfaces have demonstrated an anisotropy in the nonlinear response of the surface as it is rotated azimuthally about the surface normal. The most extensive studies of the rotational anisotropy from metals has been performed on the noble metal surfaces of (111) crystal orientation [1]. All display a sinusoidal response which is three-fold symmetric, consistent with the symmetry of the surface region and the presence of three mirror planes perpendicular to the surface. When the applied field bisects two of these planes the SHG polarization is a maximum. Figure 1, from Wong and Richmond [2], illustrates this effect for Ag(111) under the indicated conditions. All responses can be described in terms of a polarization comprised of isotropic and anisotropic terms which contain the pertinent nonlinear susceptibility tensors and Fresnel coefficients.

The anisotropy observed from noble metal surfaces is not unexpected from symmetry arguments, but is surprising because of the free-electron and, therefore, isotropic nature of the metal. Anisotropy has also been observed by Janz et al. [3] and by Plummer and his collaborators [4,5] on the (111) surface of Al, a nearly free-electron metal. While many theoretical papers on SHG have appeared, they generally address either the out of plane response of specific surfaces, the approach taken by Inglesfield [6], or have used a jellium model which can not have anisotropy due to rotational symmetry [1,7].

It was first suggested by Tom and Aumiller [8] that the rotational anisotropy was a result of interband transitions. This idea was expanded upon experimentally by Bradley, Georgiadis, Kevan and Richmond [9] and theoretically by Jiang, Payer and Burstein [10] and Petukhov and Liebsch [11]. To test whether interband transitions were the source of anisotropy, Wong and Richmond [2] examined the SHG response from Au(111) and Ag(111) at frequencies below any resonant coupling to interband transitions and found that the anisotropy not only persisted in the absence of any resonances, but also that both the phase and intensity converge to constant values.

Petukhov [12] proposed that the source of the anisotropy is a bulk quadrupolar contribution from electrons at the Fermi level. While Petukhov's theory provides a possible source for the observed anisotropy, it fails to address the role of surface electronic structure as well as the nature of screening at the surface in the low frequency limit. Presumably, at a frequency below the plasma resonance, the primary and the harmonic are screened by the metal so that the applied field does not extend beyond the first few layers, and, furthermore, any SHG that is generated in the bulk will not be transmitted back out of the solid. This is relevant to close packed surfaces such as the (111) surface of an fcc structure, because each layer, by itself, is centrosymmetric. When more than one layer is considered, the symmetry is reduced to 3-fold symmetry which is not centrosymmetric in the plane.

It is the non-resonant, "perfect screening" limit that is addressed in this Letter. First, the theoretical framework for calculating nonlinear polarizations is presented. Following this, it is shown how various responses can be analyzed in the context of a moment expansion. This moment expansion is used to demonstrate how a single s-band model is inadequate to describe the phenomenon. Finally, calculations that vary the s-d hybridization show how this coupling can explain the anisotropic polarizations for noble metals and related systems.

When calculating the electronic response of a system, the symmetries of the system and the added restrictions imposed by the applied fields must be taken into account. While it may be possible to do this via a k-space formalism, it is simplest to employ real space techniques, namely the recursion method [13,14], because this allows calculations to be done without any symmetry restrictions. Since experiments are done in the low frequency limit, the Adiabatic Approximation in which the electrons remain in their ground state with respect to the applied field is appropriate.

The recursion method calculates the projected density of states (PDOS), which is defined as the projection of the total density of states onto the orbital ϕ .

$$n_{\phi}(E) = \sum_{\alpha} |\langle \phi | \Psi_{\alpha} \rangle|^2 \delta(E - E_{\alpha}) \quad (1)$$

This is done by first transforming the quantum mechanical Hamiltonian into a tridiagonal matrix,

$$\begin{bmatrix} a_0 & b_1 & 0 & 0 & \dots \\ b_1 & a_1 & b_2 & 0 & \dots \\ 0 & b_2 & a_2 & b_3 & \dots \\ 0 & 0 & b_3 & a_3 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} \quad (2)$$

whose elements are used to construct the continued fraction representation for the PDOS

$$n_\phi(E) = \frac{1}{E - a_0 - \frac{b_1^2}{E - a_1 - \frac{b_2^2}{E - a_2 - \dots}}} \quad (3)$$

The PDOS is a useful quantity, because from this the occupation of an orbital ϕ can be calculated as a function of the applied field, λV .

$$N_\phi(\lambda V) = \int_{-\infty}^{E_{fmax}} n_\phi(E, \lambda V) dE \quad (4)$$

Once the occupation of an orbital is calculated, it must be multiplied by the position vector to obtain the polarization. The integrand in Eq. 4 can be expanded in a power series in λV and then the first three terms of this series integrated to obtain the ground state, linear, and SHG contributions of the polarization.

$$\bar{P}(\bar{E}) = \bar{P}_0 + \chi^{(1)} \cdot \bar{E} + \chi^{(2)} : \bar{E}\bar{E} + \dots \quad (5)$$

However, numerical derivatives of the total polarization gives better estimates of the susceptibilities than analytic differentiation, possibly because the numerical derivatives are the differences of quantities that are known to converge. The geometric interpretation of this integral is illustrated in Figure 2, which shows how the PDOS is shifted to higher (lower) energy with a positive (negative) field. The contribution to SHG from orbital ϕ is then related to the areas I and II in Fig. 2 which can be seen from the relations

$$\begin{aligned} P^{(2)} &= \frac{\partial^2}{\partial(\lambda V)^2} P \equiv \bar{R} \frac{N(\lambda V_+) - 2N(0) + N(\lambda V_-)}{(\lambda V_+ - \lambda V_-)^2} \\ &\equiv \bar{R} \frac{\text{Area(I)} - \text{Area(II)}}{(\lambda V_+ - \lambda V_-)^2} \end{aligned} \quad (6)$$

The linear polarization, which depends on the first derivative, is proportional to the sum of these areas rather than the difference. These areas depend not only on the Hamiltonian of the system but also depend strongly on the Fermi level. The contribution to SHG from an orbital can be positive or negative, and can even vanish depending on the position of the Fermi level.

A complete solution of a surface subject to an external electric field requires the simultaneous solutions of Schrodinger's and Poisson's equations. Inglesfield [6] has done this via a self-consistent method for the Ag(001) surface and has shown that an applied field is screened in the first atomic layer at low frequencies. Because the external field does not penetrate beyond the first centrosymmetric layer, Inglesfield's results indicate that an electronic coupling to the lower layers is necessary to explain the observed anisotropy. In the perfect screening limit, anisotropy involves a polarization at the surface that is modified by the electronic wavefunction from subsurface layers. This is in contrast to the usual non-local response in electromagnetism where a field is applied to one region and it induces a polarization in another and which can arise either from a quantum mechanical coupling or through a change in the charge density. This non-local quantum mechanical response is best understood via a moment expansion for the PDOS.

While the continued fraction (Eq. 3) is a numerically stable expansion of the projected densities of states, it is often necessary to look at the related moment expansion to gain insight into the physical processes that contribute to the PDOS. This expansion in moments was introduced by Cyrot-Lackmann [15] and the equivalence of the continued fraction and the moment expansions is discussed in the review articles by Heine [13] and Haydock [14]. The moment expansion is written

$$n_{\phi}(E) = \frac{1}{E} + \frac{\mu_1}{E^2} + \frac{\mu_2}{E^3} + \dots \quad (7)$$

where the nth moment is

$$\mu_n = \langle \phi | H^n | \phi \rangle \quad (8)$$

$$= \sum_{\alpha_1, \dots, \alpha_{n-1}} \langle \phi | H | \phi_{\alpha_1} \rangle \langle \phi_{\alpha_1} | H | \phi_{\alpha_2} \rangle \dots \langle \phi_{\alpha_{n-1}} | H | \phi \rangle \quad (9)$$

These moments can be understood in terms of quantum path counting. By inserting the appropriate sums over complete sets of basis states, Eq. 8 can be interpreted as a weighted sum over closed paths that begin and end on orbital ϕ as seen in Eq. 9.

An estimate of the magnitude of an effect can be made by finding the first moment that contributes to the effect. While SHG can arise by the second moment, anisotropy involves paths which sample the field on the surface and also extend down to the second layer. These are much longer paths and, therefore, the anisotropic terms are expected to be smaller than the isotropic. In general, various responses interfere because a path can always be found that contains more than one type of response. This prevents the separation of SHG into various surface and bulk contributions at low frequencies.

By assuming that the applied field only affects the on-site energy of the orbitals and not the coupling between orbitals, the paths that contribute to the anisotropy for a given solution of Poisson's equation can be explicitly determined. This representation for the field is similar to Effective Hamiltonian Theories [16] which have been widely applied to periodic systems perturbed by fields with a slow spatial variation.

The paths that contribute to anisotropy in SHG from an fcc structure can be related to those which contribute to stacking fault energies in the same structure. A stacking fault is defined as a layer that does not follow the crystal stacking sequence but retains the property of being close packed. Due to the lack of angular dependence in the interactions between nearest neighbor s-orbitals, all close packed structures, including structures with stacking faults, are degenerate when only these orbitals are considered [17]. This can be seen by examining the moments of the PDOS. Since there is no variation in the bond length for all close packed structures, there is only one tight-binding parameter required, $ss\sigma$. The n th moment for these systems is then the number of paths of length n times $ss\sigma$ raised to the n th power. Because this number of paths is invariant for all close packed structures, there is no energy needed to create any number of stacking faults when only s-orbitals are considered.

For the same reason that nearest neighbor interactions between s-orbitals are inadequate to explain stacking fault energies they also fail to describe anisotropy in the perfect screening limit. Since the field does not penetrate past the first layer, the moments are independent of the position of the subsurface layers as long as they still fall on valid close packed sites. When a field not perpendicular to a mirror plane is reversed, each layer below the first could also be moved, one by one, as in a stacking fault to give the net result of a reflection about a mirror plane. This would not change the moments and, therefore, the polarization would be anti-symmetric and no SHG would result in the plane. Of course, the various isotropic contributions would still be present.

This result is equally valid for bulk resonances at the surface and s-band derived surface states; both contribute to the PDOS and, therefore, both are taken into account in a moment expansion. Also, this result is more general than the tight-binding approximation presented above. Specifically, it holds true for any orthogonal, nearest neighbor basis set that has spherically-symmetric atomic orbitals. If there was imperfect screening, there would be no anisotropic contribution from layers deeper than the screening depth.

Ducastelle and Cyrot-Lackmann [18] have calculated the moments for d-bands in hcp and fcc structures and have shown how the fourth moment is the lowest moment that contributes to stacking fault energies. For transition metals the anisotropic SHG would, therefore, depend strongly on the tight-binding d-parameters. However, as described above, the d-orbitals for noble metals do not directly contribute to SHG because they are completely filled.

Ducastelle, Cyrot-Lackmann, and Friedel [17] extended the analysis of moments to include s-orbitals and s-d hybridization and emphasized the importance of s-d mixing for stacking fault energies in noble metals. They calculate corrections to the moments for close packed structures when s-d hybridization is included. Although they do not calculate the fourth moment, they point out that the first three moments are the same for fcc and hcp. The fourth moment is the lowest moment for an s-orbital starting state that is different for

the two structures. This difference in the fourth moment is a fourth degree polynomial in $sd\sigma$ with no constant, linear or cubic terms, and demonstrates how the s-band is affected by the d-bands even when the latter are completely filled.

As mentioned above, a difference in the moments for a stacking fault is exactly what is needed for anisotropy in SHG in the perfect screening limit. Fig. 3 shows a calculation of $\chi_{xx}^{(2)}$ for a cluster of 1000 atoms each with five d-orbitals and a single s-orbital. The calculation was done by varying the s-d coupling while keeping the Fermi level fixed. The various approximations and assumptions in these calculations are summarized as follows: 1) First, an Adiabatic Approximation is made with respect to the applied field. 2) The occupation of tight-binding orbitals are calculated assuming 3) the Hamiltonian for the applied electric field is diagonal in the tight-binding basis. 4) The field is screened in the first layer. These calculations provide an estimate of the coupling parameter that is consistent with calculations of stacking fault energies and the band structure for Ag.

This result does not depend on the existence of surface states as was proposed as the source of anisotropy for Al(111) by Murphy, Yeganeh, Song, and Plummer [4]. No distinction between bulk and surface states was made in deriving these results, however, surface states contribute relatively little to SHG, because they have a small weight on the PDOS.

When applying these results to other systems, it becomes obvious that any partially filled band besides the s-band can contribute to anisotropy in SHG. For example, in the case of Al(111), this would be the 3p-orbitals. For the Al(111) surface, it has been suggested by Janz, Pedersen, and van Driel [3] that the anisotropy is due to steps or defects on the surface, but, as argued above, the anisotropy is an intrinsic feature of the surface and morphology is not needed to explain the experimental results.

At low frequencies, SHG results from the collective response of all the electrons in a partially filled band rather than from single particle excitations or Fermi surface effects. Anisotropy in optical SHG can be present even in the perfect screening limit due to the

extended nature of the electronic wavefunctions. Furthermore, in certain systems such as noble metals, the existence of the anisotropy can be traced to a single parameter, the coupling between s- and d-bands.

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Figure Captions

FIG. 1. SHG intensity from the Ag(111) electrode surface as a function of the angle of rotation under p-polarized fundamental excitation wavelength of 1530 nm, a) p-polarized SHG light, b) s-polarized SHG light.

FIG. 2. A schematic of the projected density of states as function of energy. The three curves represent the PDOS without a field, with an applied field, and with the opposite field.

FIG. 3. Magnitude of the anisotropic tensor element $\chi_{xx}^{(2)}$ as functions of the coupling between s- and d-bands, $sd\sigma$.

